arXiv:cond-mat/0607318v1 [cond-mat.supr-con] 13 Jul 2006

Improved Superconducting Properties in Bulk MgB_2 Prepared by High Energy Milling of Mg and B Powder

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Abstract. The MgB_2 bulks were prepared by high energy milling of Mg and B powder. The correlations among milling times, microstructure and superconducting properties were investigated in MgB_2 bulks. Samples were characterized by x-ray diffraction (XRD), energy dispersive spectrometry (EDX) and scanning electron microscope (SEM), and the magnetization properties were examined by a Superconducting quantum interfere device (SQUID) magnetometer. It showed that the high energy milling is an effective approach to get fine crystalline (40-100nm) bulk MgB_2 with good grain connectivity and high J_c performance. The critical current density reaches to 2.0×10^6A/cm^2 at 15K and 0.59T, 5.7×10^5A/cm^2 at 2T and 3.0×10^4A/cm^2 at 5T.

PACS numbers: 74.70.Ad, 74.62.Bf, 74.25.Qt, 74.25.Sv, 74.50.+r, 74.70.-b

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1. Introduction

The improvement of the intrinsic properties of MgB_2 was recognized as a decisive goal to enable potential applications[1]. Conventional powders and sintered polycrystalline bulk MgB_2 samples typically exhibit deteriorated superconducting properties due to weak pinning[2-3]. The mechanically alloyed (MA) samples have about 1000 times smaller grains than hot deformed samples and samples sintered at high pressure[4]. The observed increased $H_{irr}(T)$ and high $J_c(H)$ manifest improved flux pinning of MA samples, which attribute to small grains and the enhanced number of grain boundaries for the nanocrystalline material[4]. It has been demonstrated before that the nanocrystalline sample has distinctly higher irreversibility fields than the bulk sample with micrometer-sized grains, especially at the low temperature[5]. One possible reason for the strong pinning found for thin films as well is their small grain size of about 10nm[5]. The mechanical alloying (MA) technique for MgB_2 powder preparation is expected for obtaining enhanced magnetic flux pinning by microstructure refinement. However, it costs as long as 20 100h[4,6,7 -12] for in situ MA precursor powder preparation. The use of short-time unalloyed high energy milling of Mg and B powder as precursor material represents an efficient combination between conventional powder preparation and mechanical alloying techniques. Agate milling media was chosen for dispelling the bad effect of the impurities. Additionally, MgB_2 is a line compound[13] and a certain deviation of the stoichiometry lead to substantially increased critical current densities compared to the stoichiometric composition[11]. The precursor powder with a Mg excess of 5was employed according to the literature[11,14-16].

2. Experimental details

Mg (99.8%) and amorphous B (95%) powder with 5were filled under purified Ar-atmosphere into an agate milling container and milling media. The milling was performed on a SPEX 8000M mill for different times t_m =1, 5, 10h using a ball-to-powder mass ratio of 3. The milled powders were then cold pressed to form pellets with a diameter of 20mm and a height of 3mm. The pellets were placed in an alumina crucible inside a tube furnace under ultra-high purity Ar-atmosphere. The heat treatment parameters were optimally chosen at 750 and 1h from our previous work[17], then cooled down to the room temperature.

The phase compositions of the samples were characterized by the APD1700 X-ray diffraction instrument. The surface morphology and microstructures of the samples were characterized by the JSM-6460 and the JSM-6700F scanning electron microscope.

A SQUID magnetometer by Quantum Design was used to measure the AC magnetic susceptibility of the samples over a temperature range of 5 to 50 K under an applied field of 1Oe. Magnetization versus magnetic field (M-H) curves were also measured on rectangular-shaped samples at temperatures of 10K and 15K under magnetic fields up to 90000Oe to determine the critical current density $J_c(H)$.

3. Results and discussion

XRD and EDX analysis reveal the appearance of a small amount of MgO impurity for both as-milled and sintered samples. The relative percentage composition of MgO phase is gradually increased with prolonged milling time for both samples. It is most probably because of the oxide diffusing into the grain surfaces during the particle reduction process and unavoidable oxygen traces during the sintering process.

The microstructures of the investigated samples are shown in Fig.1. Scanning electron microscope images mainly show spherical grains of about 40 100 nm in size for 5h milled sample. The impurity phases are evidently observed for sample milling for 10h, as marked by black arrows. Fig.2 indicates the distribution of the second phases for differently milled bulk MgB_2. There are a few small dark grey impurity phases for the sample milling for 1h. The sample milling for 5h has few impurity phases. However, there are a large number of stripped impurity phases for the sample milling for 10h.

The magnetic field dependence of magnetization for samples milling for different times is shown in Fig.3. $J_c(H)$ was calculated by Bean critical state model from magnetization curves (see Fig.4). Shown in inset is the irreversible field as a function of milling time. H_{irr} values were determined from the closure of hyseresis loops with a criterion of J_c=10^2A/cm^2[18]. As we can see, the sample milling for 5h has a significantly higher H_{irr} and J_c than the other samples in magnetic field. The critical current density reach to 2.0×10^6A/cm^2 at 15K and 0.59T, 5.7×10^5A/cm^2 at 2T and 3.0×10^4A/cm^2 at 5T. The improved pinning of this material seems to be caused by enhanced grain boundary pinning provided by the large number of grain boundaries in the sample.

The maximum J_c was not firstly discovered in MgB_2 from ball milled precursor powder. Flukiger's group[19] declaimed that J_c of ex situ Fe/MgB_2 tapes with ball milled powder first shows an enhancement for a particles size of 3/30m, followed by a decrease for further reductions to 1.5/10m and 1m. They thought that the maximum of J_c is a compromise between enhanced flux pinning at the grain boundaries, caused by these chemical impurities at a nanoscale and a decrease of J_c, caused by the introduction of too many impurities, reducing percolation of the current. However, O. Perner's group[10] considered there are two competing processes taking place during the high-energy milling. The first one initiates an improvement of the superconducting properties of bulk MgB_2. It attributes to the grain refinement resulting in a higher reactivity and, therefore, an optimal grain connectivity and high density of grain boundaries in MgB_2 bulks. The second process is expected to be the introduction of oxygen from the working atmosphere with increasing milling time, causing increased content of impurity phases with a reduced grain connectivity. The experimental data of ours are evidently in support of O. Perner's opinion from IFW Dresden.

Fig.5 shows field dependence of the volume pinning force $F_p(H)$ at 15K for samples heated at 750 °c and milled for different times. $F_p(H)$ is normalized by the maximum volume pinning force $F_{p.max}$ at the same temperature and for different milling times. The shapes of these profiles depend on the milling time. For 5h milled sample,

the $F_p(H)/F_{p.max}$ values were obviously larger than those of other samples over 1T, indicating enhanced flux pinning in high field region. The $F_{p.max}$ values of 1h and 5h milled samples reach 11.3 and 13.4GNm^{-3} at 15K. These values are nearly in the range of those commercial superconductors, NbTi and Nb_3Sn, which show 15 30GNm^{-3} at 4.2K[20].

Figure 6 shows a comparison of magnetic $J_c(H)$ for a 5h milled sample with data reported in literature[21-25]. J_c for this sample exhibits a better field performance and higher values of J_c. In the magnetic field lower than 3.5T, our 5h milled sample shows the highest J_c in 15K. The best J_c for the 5h milled sample was 2.3×10^5A/cm^2 at 3T and 15K, which exceeds the J_c values of state-of-the-art Ag/Bi-2223 tapes. Our 5h milled MgB_2 sample is even comparable with SiC doped MgB_2 bulks by Dou's group[23], which had exhibited the strongest reported flux pinning and the highest J_c in high fields to date.

In conclusion, we succeeded in preparing high critical current density bulk MgB_2 by high energy ball-milling technique. It demonstrated that it is an effective approach to get fine crystalline bulk MgB_2 with good grain connectivity and extraordinary high J_c performance. The flux pinning is enhanced in our sample by a large number of grain boundaries. Further improvement is expected to be in doped samples using high energy ball-milling technique.

4. Acknowledgment

This work was partially supported by National Natural Science Foundation project (Contract No. 50472099) and National Basic Research Program of China (Contract No. 2006CB601004).

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Figure captions

Fig.1 Fig.1 The SEM photograph of the MgB_2 bulks for different milling times: (a) 1h (b) 5h (c) 10h.

Fig.2 The distribution of the second phase in bulk MgB2 for different milling times: (a) 1h (b) 5h (c) 10h.

Fig.3 Magnetization M as a function of magnetic field H at 15K for the samples heated at 750 °c and milled for different times.

Fig.4 Magnetization critical current density J_c as a function of magnetic field H at 15 K for the samples heated at 750 °c and milled for different times. Shown in inset is the irreversible field as a function of milling time. H_{irr} values were determined from the closure of hyseresis loops with a criterion of J_c=10^2A/cm^2[18].

Fig.5 Field dependence of the volume pinning force $F_p(H)$ at 15K for samples heated at 750 °c and milled for different times. $F_p(H)$ is normalized by the maximum volume pinning force $F_{p.max}$ at the same temperature and milling time.

Fig.6 A comparison of magnetic $J_c(H)$ for our 5h milled sample and for samples that were: MA with C doping by Uni. Of WM(see Ref. 21),MA with 5% Mg Surplus by IFW(see Ref. 22), undoped (see Ref. 23) and doped samples(see Ref. 23-25) by Dou's group.

Fig.1

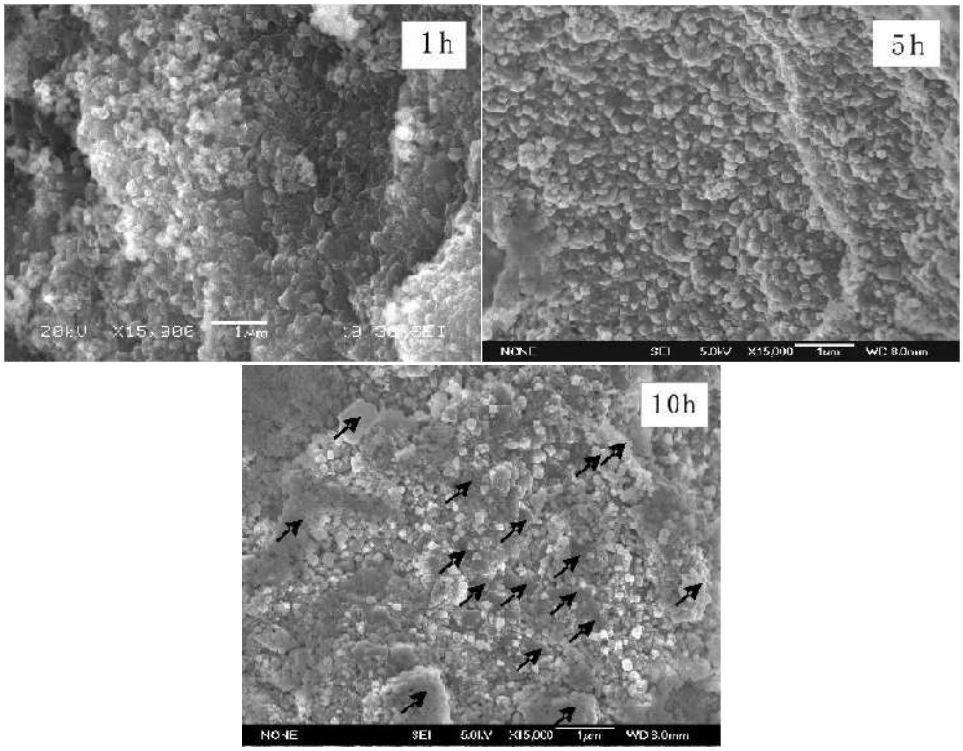


Fig.2

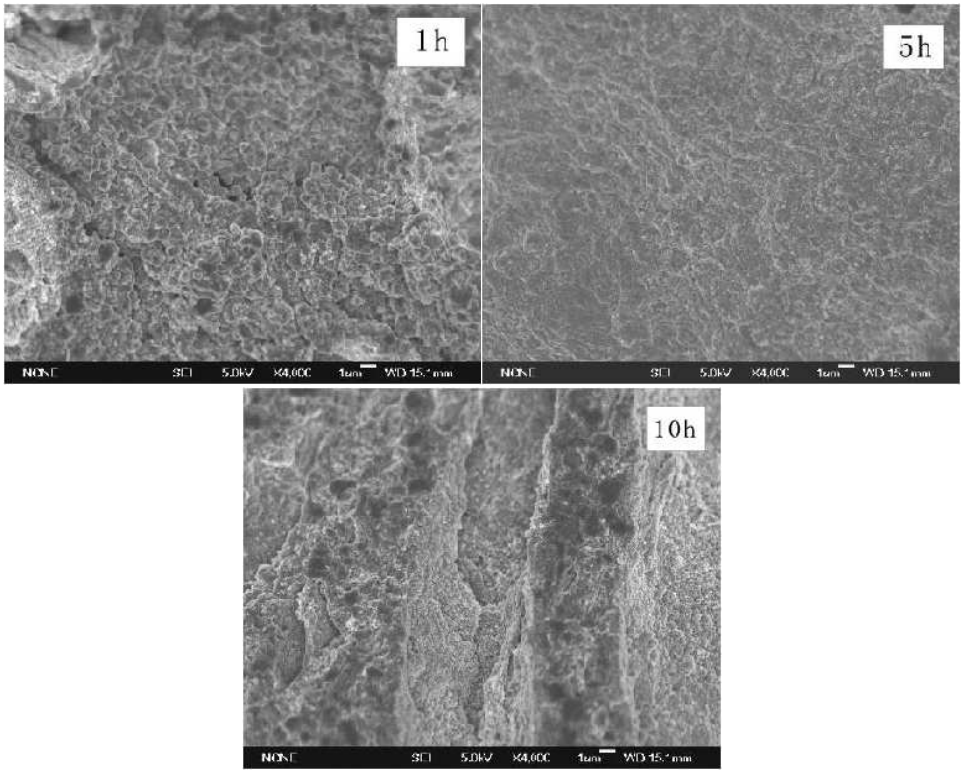


Fig.3

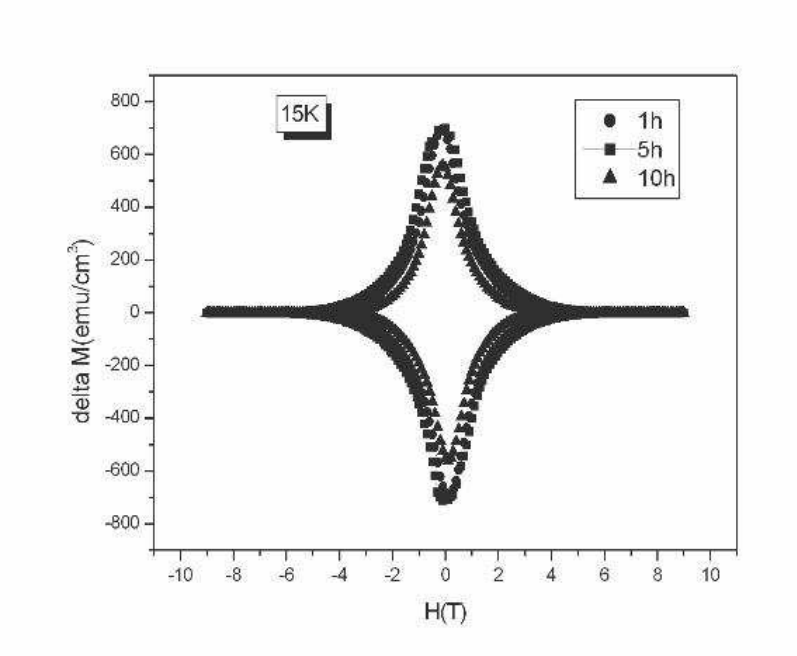

15K
1h
5h
10h
delta M(emu/cm^3)
H(T)
800
600
400
200
0
-200
-400
-600
-800
-10
-8
-6
-4
-2
0
2
4
6
8
10

Fig.4

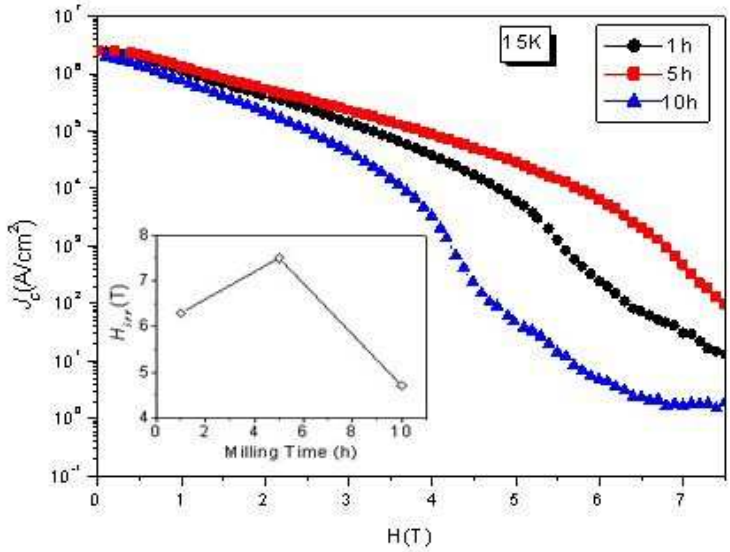


Fig.5

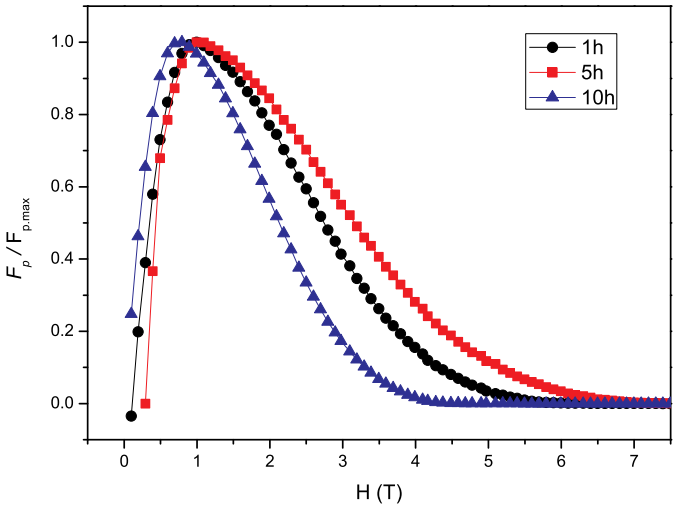
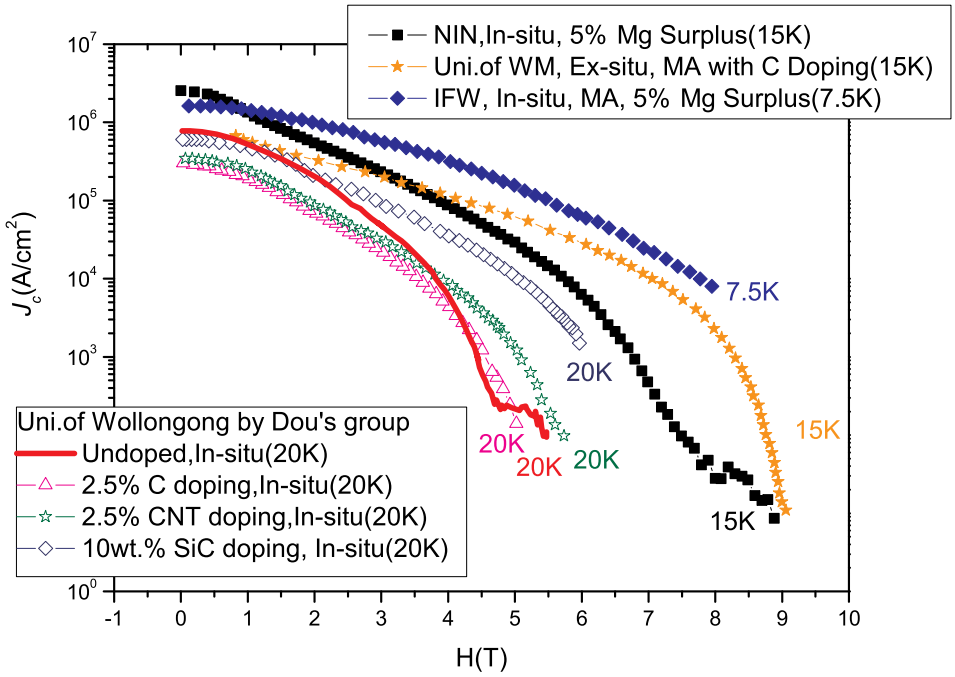


Fig.6


NIN,In-situ, 5% Mg Surplus(15K)
Uni.of WM, Ex-situ, MA with C Doping(15K)
IFW, In-situ, MA, 5% Mg Surplus(7.5K)
Uni.of Wollongong by Dou's group
Undoped,In-situ(20K)
2.5% C doping,In-situ(20K)
2.5% CNT doping,In-situ(20K)
10wt.% SiC doping, In-situ(20K)
7.5K
20K
15K
20K
20K
20K
15K
J_c (A/cm^2)
H(T)